

DEVELOPMENT OF ELECTROCHEMICAL
BIOSENSOR BASED ON SnO_2 -NANOFIBER
WITH ENHANCED ELECTRON TRANSFER OF
REDOX BIOMOLECULE

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at University Malaysia Pahang or any other institutions.

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ABSTRAK

Biosensor jenis elektrokimia sangat sesuai untuk pemantauan kandungan H_2O_2 , glukosa, kolesterol, petanda barah, penyakit berjangkit berkaitan, dan sebagainya. Tetapi pembangunan biosensor elektrokimia dengan enzim pautan mengalami cabaran besar seperti kekurangan gandingan elektronik yang baik dan hubungan elektrik di antara tapak aktif protein / enzim redoks yang digunakan dan permukaan elektrod. Oleh itu sebagai satu jalan penyelesaian, banyak usaha telah nanofiber (NF) SnO_2 sebagai bahan nano terunggul dalam biosensor. Usaha utama disertasi ini adalah untuk menguji peranan kritikal yang dimainkan oleh bahan nano tersebut apabila ia digunakan dalam pembangunan biosensor elektrokimia dengan cara immobilisasikan protein redoks atau enzim yang berbeza. SnO_2 -NF yang digunakan dalam penyelidikan ini disintesis dengan cara teknik elektrospinning dari prekursor timah. Campuran SnO_2 -NF yang disintesis meningkatkan kecekapan muatan biomolekul kerana kawasan permukaan yang tinggi tercapai. Morfologi nanofiber yang disintesis juga telah dinilai oleh mikroskop elektron pengimbasan emisi lapangan (FESEM) dan spektrometer sinaran sinar-X (EDX). Sebelum ini, biosensor H_2O_2 amperometri telah direka berdasarkan enzim “horseradish peroxidase” (HRP) dengan NF SnO_2 diletak pada permukaan elektrod karbon gelas (GC) dengan menggunakan “chitosan”, yang didapati bertindak balas cepat iaitu dengan had pengesanan yang lebih rendah iaitu $0.3 \mu\text{M}$ ($S/N=3$). Biosensor HRP/ SnO_2 -NFs/Ch/GCE yang direka menunjukkan lineariti antara kepekatan 10 hingga $120 \mu\text{M}$ H_2O_2 . Untuk menilai prestasi nanofiber SnO_2 yang diubahsuai dalam biosensor, biosensor H_2O_2 berasaskan HRP kemudian pula direka, yang mana NF dengan SnO_2 telah di polimerisasi dengan polyaniline (PANI) dan enzim HRP telah dimobilisasi dengan PANI/ SnO_2 ini ke permukaan GC. Biosensor HRP/PANI/ SnO_2 -NF/Ch/GC ini yang direka membuat tindak balas amperometri linear ke arah kepekatan H_2O_2 dari julat 10 hingga $80 \mu\text{M}$ dengan nilai had pengesanan $0.133 \mu\text{M}$ ($S/N=3$). Biosensor pengesanan glukosa dengan guna enzim kemudian direka dan rekaan berdasarkan SnO_2 -NF dengan polimer bersama glukosa oksidase (GOx) dan horseradish peroxidase (HRP) dengan ini dengan menggunakan chitosan ke elektrod karbon kaca. Biosensor ini direka untuk menilai potensi keupayaan SnO_2 -NFs dalam pembangunan biosensor dengan dua jenis bi-enzim. Biosensor HRP-GOx/PANI/ SnO_2 -NF/Ch/GCE memaparkan tindak balas amperometri linear ke arah kepekatan glukosa antara 10 hingga $110 \mu\text{M}$ dengan had pengesanan sebanyak $1.8 \mu\text{M}$ ($S/N=3$). Aktiviti anti-perencatan juga disiasat. Akhirnya, SnO_2 -NF dengan tiub nano karbon (CNTs) dan chitosan digunakan bersama untuk fabrikasi biosensor H_2O_2 terunggul lain untuk menilai kesan sinergi SnO_2 -NFs dengan bahan nano lain dalam biosensing. Protein redoks (Hemoglobin) telah dimobilisasi dengan nanocomposite CNT/ SnO_2 -NF dengan menggunakan chitosan di permukaan GC. Elektrod Hb/CNT/ SnO_2 -NF/Ch/GC yang dihasilkan efektif kepada kepekatan H_2O_2 dalam pelbagai antara 10 hingga $200 \mu\text{M}$ dan had pengesanan paling rendah ialah 30 nM ($S/N=3$). Didapati pemindahan elektron langsung antara pusat aktif protein/enzim redoks dan permukaan elektrod telah terhasil dengan jayanya kerana menggunakan nanofiber ini dan semua biosensor yang dilaporkan dalam kerja ini mempamerkan keupayaan selektiviti yang sangat baik juga kestabilan, dan kebolehulangan.

ABSTRACT

Electrochemical biosensors are highly desirable for the monitoring of H_2O_2 , glucose, cholesterol, cancer biomarkers, infectious diseases, etc. But the development of enzymatic electrochemical biosensors is oppressed with great challenges like the lack of good electronic coupling and electrical contact between the active site of the used redox protein/enzyme and the electrode surface. Hence, a great deal of effort has been devoted by using nanofiber (NF) of SnO_2 as nanomaterial in biosensor to deal with this challenge. Thus, the main theme of this dissertation pertains to highlighting the critical roles that are played by this nanomaterial when this is applied in the development of electrochemical biosensors by immobilizing different redox proteins or enzymes. The SnO_2 -NFs used in this research was synthesised by electrospinning technique from the tin precursor. The synthesized SnO_2 -NF increases the efficiency of biomolecule loading due to its high surface area. The morphology of the nanofiber was evaluated by field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray (EDX) spectrometer was used for evaluating the sterility of the synthesized nanofiber. For this research project, an amperometric H_2O_2 biosensor was designed and fabricated firstly based on the immobilization of horseradish peroxidase (HRP) enzyme with NF of SnO_2 onto the surface of glassy carbon electrode (GC) by using chitosan, which exhibited fast response with lower detection limit of $0.3 \mu\text{M}$ ($S/N=3$). The fabricated HRP/ SnO_2 -NF/Ch/GC biosensor showed linearity ranges between the concentration of 10 to $120 \mu\text{M}$ H_2O_2 . To evaluate the performance of the modified SnO_2 nanofiber in biosensor, a HRP based H_2O_2 biosensor was then designed and fabricated, whereas, the NFs of SnO_2 was polymerized with polyaniline (PANI) and HRP enzyme was immobilized with this PANI/ SnO_2 onto the surface of GC. The fabricated HRP/PANI/ SnO_2 -NF/Ch/GCE biosensor displayed a linear amperometric response towards the H_2O_2 concentration range from 10 to $80 \mu\text{M}$ with a detection limit of $0.133 \mu\text{M}$ ($S/N=3$). A bienzymatic glucose biosensor was then designed and fabricated based on the polymerized SnO_2 -NF via co-immobilization of glucose oxidase (GOx) and horseradish peroxidase (HRP) with this by using chitosan onto glassy carbon electrode. This biosensor was fabricated to evaluate the potentiality of SnO_2 -NF in the development of bienzymatic biosensor. The HRP-GOx/PANI/ SnO_2 -NF/Ch/GC biosensor displayed a linear amperometric response towards the glucose concentration range from 10 to $110 \mu\text{M}$ with a detection limit of $1.8 \mu\text{M}$ ($S/N=3$). Also the anti-interference activity was investigated. Finally, SnO_2 -NF with Carbon nanotubes (CNT) and chitosan was used together for the fabrication of another novel H_2O_2 biosensor to evaluate the synergic effect of SnO_2 -NF with other nanomaterial in biosensing. A redox protein (Hemoglobin) was immobilized with CNT/ SnO_2 -NF nanocomposite by using chitosan on the surface of GC. The fabricated Hb/CNT/ SnO_2 -NF/Ch/GC electrode exhibited linearity to the H_2O_2 concentration in a wide range of 10 to $200 \mu\text{M}$ and the lower detection limit was 30 nM ($S/N=3$). A direct electron transfer between the active center of redox protein/enzyme and the electrode surface was established because of using this nanofiber and all the biosensors reported in this work exhibited excellent selectivity with stability, reproducibility and repeatability.

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LIST OF SYMBOLS

A	Geometric area of the working electrode
C	Concentration
E_0	Formal potential
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
I	Current
I_{max}	Maximum current
I_p	Peak current
I_{ss}	Steady state current
K_m	Michaelis–Menten constant
k_s	Interfacial electron transfer rate constants
n	Number of transferred electrons
v	Scan rate
S	Signal
N	Noise

LIST OF ABBREVIATIONS

LOD	Limit of Detection
RSD	Relative standar deviation
FESEM	Field Emission Scanning Electron Microscopy
CV	Cyclic Voltammetry
SEM	Scanning Electron Microscopy
HRP	Horseradish peroxidase
GOx	Glucose oxidase
EDX	Energy-dispersive X-ray spectroscopy

REFERENCES

- Alim, S., Jaya Vejayan, P., & AKM, K. (2018). Direct Electrochemistry of Catalase Immobilized at Polymerized-SnO₂ Multiporous Modified Electrode for an Amperometric H₂O₂ Biosensor. *Biomedical Journal of Scientific and Technical Research*, 3(4), 1-6.
- Alim, S., Kafi, A. K. M., Jose, R., Yusoff, M. M., & Vejayan, J. Enhanced direct electron transfer of redox protein based on multiporous SnO₂ nanofiber-carbon nanotube nanocomposite and its application in biosensing. *International Journal of Biological Macromolecules*.
- Baghayeri, M., Rouhi, M., Lakouraj, M. M., & Amiri-Aref, M. (2017). Bioelectrocatalysis of hydrogen peroxide based on immobilized hemoglobin onto glassy carbon electrode modified with magnetic poly (indole-co-thiophene) nanocomposite. *Journal of Electroanalytical Chemistry*, 784, 69-76.
- Baghayeri, M., & Veisi, H. (2015). Fabrication of a facile electrochemical biosensor for hydrogen peroxide using efficient catalysis of hemoglobin on the porous Pd@ Fe₃O₄-MWCNT nanocomposite. *Biosensors and Bioelectronics*, 74, 190-198.
- Baghayeri, M., Veisi, H., & Ghanei-Motlagh, M. (2017). Amperometric glucose biosensor based on immobilization of glucose oxidase on a magnetic glassy carbon electrode modified with a novel magnetic nanocomposite. *Sensors and Actuators B: Chemical*, 249, 321-330.
- Baghayeri, M., Zare, E. N., & Hasanzadeh, R. (2014). Facile synthesis of PSMA-g-3ABA/MWCNTs nanocomposite as a substrate for hemoglobin immobilization: application to catalysis of H₂O₂. *Materials Science and Engineering: C*, 39, 213-220.
- Baghayeri, M., Zare, E. N., & Lakouraj, M. M. (2014). A simple hydrogen peroxide biosensor based on a novel electro-magnetic poly (p-phenylenediamine)@ Fe₃O₄ nanocomposite. *Biosensors and Bioelectronics*, 55, 259-265.
- Balamurugan, J., Thanh, T. D., Karthikeyan, G., Kim, N. H., & Lee, J. H. (2016). A novel hierarchical 3D N-Co-CNT@ NG nanocomposite electrode for non-enzymatic glucose and hydrogen peroxide sensing applications. *Biosensors and Bioelectronics*.
- Bankar, S. B., Bule, M. V., Singhal, R. S., & Ananthanarayan, L. (2009). Glucose oxidase — An overview. *Biotechnology advances*, 27(4), 489-501.
- Barsan, M. M., Ghica, M. E., & Brett, C. M. (2015). Electrochemical sensors and biosensors based on redox polymer/carbon nanotube modified electrodes: a review. *Analytica Chimica Acta*, 881, 1-23.

- Benvenuto, P., Kafi, A. K. M., & Chen, A. (2009). High performance glucose biosensor based on the immobilization of glucose oxidase onto modified titania nanotube arrays. *Journal of Electroanalytical Chemistry*, 627(1), 76-81.
- Boujakhrou, A., Díez, P., Sánchez, A., Martínez-Ruiz, P., Pingarrón, J. M., & Villalonga, R. (2016). Gold nanoparticles-decorated silver-bipyridine nanobelts for the construction of mediatorless hydrogen peroxide biosensor. *Journal of Colloid and Interface Science*, 482, 105-111.
- Bui, T. T., & Park, S.-Y. (2016). A carbon dot-hemoglobin complex-based biosensor for cholesterol detection. *Green Chemistry*, 18(15), 4245-4253.
- Cammann, K. (1977). Bio-sensors based on ion-selective electrodes. *Fresenius' Zeitschrift für Analytische Chemie*, 287(1), 1-9.
- Charoensirithavorn, P., Ogomi, Y., Sagawa, T., Hayase, S., & Yoshikawa, S. (2009). A facile route to TiO₂ nanotube arrays for dye-sensitized solar cells. *Journal of Crystal Growth*, 311(3), 757-759.
- Chen, J., Li, C., Xu, F., Zhou, Y., Lei, W., Sun, L., & Zhang, Y. (2012). Hollow SnO₂ microspheres for high-efficiency bilayered dye sensitized solar cell. *RSC Advances*, 2(19), 7384-7387.
- Chen, M., Hou, C., Huo, D., Yang, M., & Fa, H. (2016). An ultrasensitive electrochemical DNA biosensor based on a copper oxide nanowires/single-walled carbon nanotubes nanocomposite. *Applied Surface Science*, 364, 703-709.
- Chen, X., Hu, N., Zeng, Y., Rusling, J. F., & Yang, J. (1999). Ordered electrochemically active films of hemoglobin, didodecyldimethylammonium ions, and clay. *Langmuir*, 15(20), 7022-7030.
- Chu, D., Masuda, Y., Ohji, T., & Kato, K. (2011). Fast synthesis, optical and bio-sensor properties of SnO₂ nanostructures by electrochemical deposition. *Chemical Engineering Journal*, 168(2), 955-958.
- Cui, D., Zheng, Z., Peng, X., Li, T., Sun, T., & Yuan, L. (2017). Fluorine-doped SnO₂ nanoparticles anchored on reduced graphene oxide as a high-performance lithium ion battery anode. *Journal of Power Sources*, 362, 20-26.
- Dalkıran, B., Erden, P. E., & Kılıç, E. (2017). Amperometric biosensors based on carboxylated multiwalled carbon nanotubes-metal oxide nanoparticles-7, 7, 8, 8-tetracyanoquinodimethane composite for the determination of xanthine. *Talanta*, 167, 286-295.
- Deng, S.-Y., Zhang, G.-Y., Shan, D., Liu, Y.-H., Wang, K., & Zhang, X.-J. (2015). Pyrocatechol violet-assisted in situ growth of copper nanoparticles on carbon

- nanotubes: The synergic effect for electrochemical sensing of hydrogen peroxide. *Electrochimica Acta*, 155, 78-84.
- Devasenathipathy, R., Mani, V., Chen, S.-M., Huang, S.-T., Huang, T.-T., Lin, C.-M., Hwa, K.-Y., Chen, T.-Y., & Chen, B.-J. (2015). Glucose biosensor based on glucose oxidase immobilized at gold nanoparticles decorated graphene-carbon nanotubes. *Enzyme and Microbial Technology*, 78, 40-45.
- Dhand, C., Das, M., Datta, M., & Malhotra, B. (2011). Recent advances in polyaniline based biosensors. *Biosensors and Bioelectronics*, 26(6), 2811-2821.
- Ding, J., Zhang, H., Jia, F., Qin, W., & Du, D. (2014). Assembly of carbon nanotubes on a nanoporous gold electrode for acetylcholinesterase biosensor design. *Sensors and Actuators B: Chemical*, 199, 284-290.
- Dresselhaus, M. S., Dresselhaus, G., & Eklund, P. C. (1996). *Science of fullerenes and carbon nanotubes: their properties and applications*: Academic press.
- Duan, Y., Zheng, J., Fu, N., Fang, Y., Liu, T., Zhang, Q., Zhou, X., Lin, Y., & Pan, F. (2015). Enhancing the performance of dye-sensitized solar cells: doping SnO₂ photoanodes with Al to simultaneously improve conduction band and electron lifetime. *Journal of Materials Chemistry A*, 3(6), 3066-3073.
- Dunford, H. B. (1991). Horseradish peroxidase: structure and kinetic properties. *Peroxidase in chemistry and biology*, 1-23.
- Elumalai, N. K., Jose, R., Archana, P. S., Chellappan, V., & Ramakrishna, S. (2012). Charge transport through electrospun SnO₂ nanoflowers and nanofibers: role of surface trap density on electron transport dynamics. *The Journal of Physical Chemistry C*, 116(42), 22112-22120.
- Feng, X., Cheng, H., Pan, Y., & Zheng, H. (2015). Development of glucose biosensors based on nanostructured graphene-conducting polyaniline composite. *Biosensors and Bioelectronics*, 70, 411-417.
- Fouad, O., Glaspell, G., & El-Shall, M. (2008). Growth and characterization of ZnO, SnO₂ and ZnO/SnO₂ nanostructures from the vapor phase. *Topics in Catalysis*, 47(1-2), 84-96.
- Fusco, G., Bollella, P., Mazzei, F., Favero, G., Antiochia, R., & Tortolini, C. (2016). Catalase-based modified graphite electrode for hydrogen peroxide detection in different beverages. *Journal of analytical methods in chemistry*, 2016.
- Gao, W., Tjiu, W. W., Wei, J., & Liu, T. (2014). Highly sensitive nonenzymatic glucose and H₂O₂ sensor based on Ni(OH)₂/electroreduced graphene oxide–Multiwalled carbon nanotube film modified glass carbon electrode. *Talanta*, 120, 484-490.

- Ghrera, A. S., Pandey, C. M., & Malhotra, B. D. (2018). Multiwalled carbon nanotube modified microfluidic-based biosensor chip for nucleic acid detection. *Sensors and Actuators B: Chemical*, 266, 329-336.
- Gong, Y., Chen, X., Lu, Y., & Yang, W. (2015). Self-assembled dipeptide–gold nanoparticle hybrid spheres for highly sensitive amperometric hydrogen peroxide biosensors. *Biosensors and Bioelectronics*, 66, 392-398.
- Gubbala, S., Chakrapani, V., Kumar, V., & Sunkara, M. K. (2008). Band-Edge Engineered Hybrid Structures for Dye-Sensitized Solar Cells Based on SnO₂ Nanowires. *Advanced Functional Materials*, 18(16), 2411-2418.
- Guler, M., Turkoglu, V., & Kivrak, A. (2015). A novel glucose oxidase biosensor based on poly([2,2';5',2'']-terthiophene-3'-carbaldehyde) modified electrode. *International Journal of Biological Macromolecules*, 79, 262-268.
- Guo, X. M., Zhao, J. T., Yin, X. T., & Huang, S. L. (2017). *Sensitivity and Selectivity of SnO₂-Based Sensor for CO and H₂ Detections: A Novel Method to Detect Simultaneously the CO and H₂ Concentrations*. Paper presented at the Advances in Science and Technology.
- Hajian, A., Ghodsi, J., Afraz, A., Yurchenko, O., & Urban, G. (2016). Nanomolar detection of methylparaben by a cost-effective hemoglobin-based biosensor. *Materials Science and Engineering: C*, 69, 122-127.
- Haldorai, Y., Hwang, S.-K., Gopalan, A.-I., Huh, Y. S., Han, Y.-K., Voit, W., Sai-Anand, G., & Lee, K.-P. (2016). Direct electrochemistry of cytochrome c immobilized on titanium nitride/multi-walled carbon nanotube composite for amperometric nitrite biosensor. *Biosensors and Bioelectronics*, 79, 543-552.
- Han, L., Tao, H., Huang, M., Zhang, Y., Qiao, S., & Shi, R. (2016). A hydrogen peroxide biosensor based on multiwalled carbon nanotubes-polyvinyl butyral film modified electrode. *Russian Journal of Electrochemistry*, 52(2), 115-122.
- Han, X., Huang, W., Jia, J., Dong, S., & Wang, E. (2002). Direct electrochemistry of hemoglobin in egg–phosphatidylcholine films and its catalysis to H₂O₂. *Biosensors and Bioelectronics*, 17(9), 741-746.
- Harbury, H. A. (1957). Oxidation-reduction potentials of horseradish peroxidase. *Journal of Biological Chemistry*, 225(2), 1009-1024.
- Heli, H., & Pishahang, J. (2014). Cobalt oxide nanoparticles anchored to multiwalled carbon nanotubes: Synthesis and application for enhanced electrocatalytic reaction and highly sensitive nonenzymatic detection of hydrogen peroxide. *Electrochimica Acta*, 123, 518-526.

- Hong, J., Ghourchian, H., & Moosavi-Movahedi, A. A. (2006). Direct electron transfer of redox proteins on a Nafion-cysteine modified gold electrode. *Electrochemistry communications*, 8(10), 1572-1576.
- Huang, J., Yue, G., Yang, J., Bai, S., Hu, Q., & Wang, L. (2017). Design, synthesis and application of carboxylic multi-walled carbon nanotubes/tetrahexahedral platinum nanocrystals nanocomposites biosensor for simultaneous determination of guanine and adenine in DNA. *Journal of Electroanalytical Chemistry*.
- Huang, K.-J., Liu, Y.-J., Wang, H.-B., Wang, Y.-Y., & Liu, Y.-M. (2014). Sub-femtomolar DNA detection based on layered molybdenum disulfide/multi-walled carbon nanotube composites, Au nanoparticle and enzyme multiple signal amplification. *Biosensors and Bioelectronics*, 55, 195-202.
- Hwa, K.-Y., & Subramani, B. (2014). Synthesis of zinc oxide nanoparticles on graphene-carbon nanotube hybrid for glucose biosensor applications. *Biosensors and Bioelectronics*, 62, 127-133.
- Hwang, B. W., Lee, S. C., Ahn, J. H., Kim, S. Y., Jung, S. Y., Lee, D. D., Huh, J. S., & Kim, J. C. (2017). High Sensitivity and Recoverable SnO₂-Based Sensor Promoted with Fe₂O₃ and ZnO for Sub-ppm H₂S Detection. *Journal of Nanoelectronics and Optoelectronics*, 12(6), 617-621.
- Iwuoha, E. I., Saenz de Villaverde, D., Garcia, N. P., Smyth, M. R., & Pingarron, J. M. (1997). Reactivities of organic phase biosensors. 2. The amperometric behaviour of horseradish peroxidase immobilised on a platinum electrode modified with an electrosynthetic polyaniline film. *Biosensors and Bioelectronics*, 12(8), 749-761.
- Kaçar, C., Dalkiran, B., Erden, P. E., & Kiliç, E. (2014). An amperometric hydrogen peroxide biosensor based on Co₃O₄ nanoparticles and multiwalled carbon nanotube modified glassy carbon electrode. *Applied Surface Science*, 311, 139-146.
- Kafi, A., & Crossley, M. J. (2013). Synthesis of a conductive network of crosslinked carbon nanotube/hemoglobin on a thiol-modified Au Surface and its application to biosensing. *Biosensors and Bioelectronics*, 42, 273-279.
- Kafi, A., Wu, G., & Chen, A. (2008). A novel hydrogen peroxide biosensor based on the immobilization of horseradish peroxidase onto Au-modified titanium dioxide nanotube arrays. *Biosensors and Bioelectronics*, 24(4), 566-571.
- Kafi, A., Yam, C., Azmi, N., & Yusoff, M. M. (2018). Carbonyl Functionalized Single-Walled Carbon Nanotube-Hb Crosslinked Network: A Novel Platform for Studying Bio-Electrochemistry and Electrocatalysis of Hemoglobin. *Journal of nanoscience and nanotechnology*, 18(4), 2422-2428.

- Kafi, A. K. M., Naqshabandi, M., Yusoff, M. M., & Crossley, M. J. (2017). Improved peroxide biosensor based on Horseradish Peroxidase/Carbon Nanotube on a thiol-modified gold electrode. *Enzyme and microbial technology*.
- Kafi, A. K. M., Naqshabandi, M., Yusoff, M. M., & Crossley, M. J. (2018). Improved peroxide biosensor based on Horseradish Peroxidase/Carbon Nanotube on a thiol-modified gold electrode. *Enzyme and microbial technology*, 113, 67-74.
- Kafi, A. K. M., Wali, Q., Jose, R., Biswas, T. K., & Yusoff, M. M. (2017). A glassy carbon electrode modified with SnO₂ nanofibers, polyaniline and hemoglobin for improved amperometric sensing of hydrogen peroxide. *Microchimica acta*, 184(11), 4443-4450.
- Kafi, A. K. M., Wali, Q., Jose, R., Biswas, T. K., Yusoff, M. M. (2017). A glassy carbon electrode modified with SnO₂ nanofibers, polyaniline and hemoglobin for improved amperometric sensing of hydrogen peroxide. *Microchimica acta*, 184(11), 4443-4450.
- Kausaite-Minkstimiene, A., Simanaityte, R., Ramanaviciene, A., Glumbokaite, L., & Ramanavicius, A. (2017). Reagent-less amperometric glucose biosensor based on a graphite rod electrode layer-by-layer modified with 1,10-phenanthroline-5,6-dione and glucose oxidase. *Talanta*, 171, 204-212.
- Kim, G.-S., Seo, H.-K., Godble, V., Kim, Y.-S., Yang, O.-B., & Shin, H.-S. (2006). Electrophoretic deposition of titanate nanotubes from commercial titania nanoparticles: application to dye-sensitized solar cells. *Electrochemistry communications*, 8(6), 961-966.
- Kim, I., & Choi, W. (2017). Hybrid gas sensor having TiO₂ nanotube arrays and SnO₂ nanoparticles. *International Journal of Nanotechnology*, 14(1-6), 155-165.
- Ko, S., Takahashi, Y., Fujita, H., Tatsuma, T., Sakoda, A., & Komori, K. (2012). Peroxidase-modified cup-stacked carbon nanofiber networks for electrochemical biosensing with adjustable dynamic range. *RSC Advances*, 2(4), 1444-1449.
- Kong, F.-Y., Li, W.-W., Wang, J.-Y., Fang, H.-L., Fan, D.-H., & Wang, W. (2015). Direct electrolytic exfoliation of graphite with hemin and single-walled carbon nanotube: Creating functional hybrid nanomaterial for hydrogen peroxide detection. *Analytica chimica acta*, 884, 37-43.
- Korotcenkov, G. (2013). Handbook of gas sensor materials. *Properties, Advantages and*.
- Kumar-Krishnan, S., Hernandez-Rangel, A., Pal, U., Ceballos-Sanchez, O., Flores-Ruiz, F., Prokhorov, E., de Fuentes, O. A., Esparza, R., & Meyyappan, M. (2016). Surface functionalized halloysite nanotubes decorated with silver

nanoparticles for enzyme immobilization and biosensing. *Journal of Materials Chemistry B*, 4(15), 2553-2560.

- Kumar, E. N., Jose, R., Archana, P., Vijila, C., Yusoff, M., & Ramakrishna, S. (2012). High performance dye-sensitized solar cells with record open circuit voltage using tin oxide nanoflowers developed by electrospinning. *Energy & Environmental Science*, 5(1), 5401-5407.
- Lavanya, N., Radhakrishnan, S., Sekar, C., Navaneethan, M., & Hayakawa, Y. (2013). Fabrication of Cr doped SnO₂ nanoparticles based biosensor for the selective determination of riboflavin in pharmaceuticals. *Analyst*, 138(7), 2061-2067.
- Li, J., Mei, H., Zheng, W., Pan, P., Sun, X., Li, F., Guo, F., Zhou, H., Ma, J., & Xu, X. (2014). A novel hydrogen peroxide biosensor based on hemoglobin-collagen-CNTs composite nanofibers. *Colloids and Surfaces B: Biointerfaces*, 118, 77-82.
- Li, J., Sun, Q., Mao, Y., Bai, Z., Ning, X., & Zheng, J. (2017). Sensitive and low-potential detection of NADH based on boronic acid functionalized multi-walled carbon nanotubes coupling with an electrocatalysis. *Journal of Electroanalytical Chemistry*, 794, 1-7.
- Li, L., Huang, J., Wang, T., Zhang, H., Liu, Y., & Li, J. (2010). An excellent enzyme biosensor based on Sb-doped SnO₂ nanowires. *Biosensors and Bioelectronics*, 25(11), 2436-2441.
- Li, X., Liu, X., Wang, W., Li, L., & Lu, X. (2014). High loading Pt nanoparticles on functionalization of carbon nanotubes for fabricating nonenzyme hydrogen peroxide sensor. *Biosensors and Bioelectronics*, 59, 221-226.
- Li, Y., Hodak, M., Lu, W., & Bernholc, J. (2017). Selective sensing of ethylene and glucose using carbon-nanotube-based sensors: an ab initio investigation. *Nanoscale*, 9(4), 1687-1698.
- Lin, Y., Li, L., Hu, L., Liu, K., & Xu, Y. (2014). Multifunctional poly (dopamine)-assisted synthesis of silver nano particles/carbon nanotubes nanocomposite: Toward electrochemical sensing of hydrogen peroxide with enhanced sensitivity. *Sensors and Actuators B: Chemical*, 202, 527-535.
- Lin, Y., Taylor, S., Li, H., Fernando, K. S., Qu, L., Wang, W., Gu, L., Zhou, B., & Sun, Y.-P. (2004). Advances toward bioapplications of carbon nanotubes. *Journal of Materials Chemistry*, 14(4), 527-541.
- Liu, H., Duan, C., Yang, C., Shen, W., Wang, F., & Zhu, Z. (2015). A novel nitrite biosensor based on the direct electrochemistry of hemoglobin immobilized on MXene-Ti₃C₂. *Sensors and Actuators B: Chemical*, 218, 60-66.

- Liu, H., Guo, K., Lv, J., Gao, Y., Duan, C., Deng, L., & Zhu, Z. (2017). A novel nitrite biosensor based on the direct electrochemistry of horseradish peroxidase immobilized on porous Co₃O₄ nanosheets and reduced graphene oxide composite modified electrode. *Sensors and Actuators B: Chemical*, 238, 249-256.
- Liu, S., Dai, Z., Chen, H., & Ju, H. (2004). Immobilization of hemoglobin on zirconium dioxide nanoparticles for preparation of a novel hydrogen peroxide biosensor. *Biosensors and Bioelectronics*, 19(9), 963-969.
- Liu, X., Pan, Z., Dong, Z., Lu, Y., Sun, Q., Wu, T., Bao, N., He, H., & Gu, H. (2016). Amperometric oxygen biosensor based on hemoglobin encapsulated in nanosized grafted starch particles. *Microchimica acta*, 183(1), 353-359.
- Liu, X., Yan, R., Zhang, J., Zhu, J., & Wong, D. K. (2015). Evaluation of a carbon nanotube-titanate nanotube nanocomposite as an electrochemical biosensor scaffold. *Biosensors and Bioelectronics*, 66, 208-215.
- Liu, X., Yan, R., Zhang, J., Zhu, J., & Wong, D. K. Y. (2015). Evaluation of a carbon nanotube-titanate nanotube nanocomposite as an electrochemical biosensor scaffold. *Biosensors and Bioelectronics*, 66, 208-215.
- Liu, Y., Gong, J., Wu, W., Fang, Y., Wang, Q., & Gu, H. (2016). A novel bio-nanocomposite based on hemoglobin and carboxyl graphene for enhancing the ability of carrying oxygen. *Sensors and Actuators B: Chemical*, 222, 588-597.
- Liu, Y., Han, T., Chen, C., Bao, N., Yu, C.-M., & Gu, H.-Y. (2011). A novel platform of hemoglobin on core-shell structurally Fe₃O₄@Au nanoparticles and its direct electrochemistry. *Electrochimica Acta*, 56(9), 3238-3247.
- Liu, Y., Liu, X., Guo, Z., Hu, Z., Xue, Z., & Lu, X. (2017). Horseradish peroxidase supported on porous graphene as a novel sensing platform for detection of hydrogen peroxide in living cells sensitively. *Biosensors and Bioelectronics*, 87, 101-107.
- Liu, Z., Wang, J., Xie, D., & Chen, G. (2008). Polyaniline-Coated Fe₃O₄ Nanoparticle-Carbon-Nanotube Composite and its Application in Electrochemical Biosensing. *Small*, 4(4), 462-466.
- Lojestani, F., Shahnava, Z., Mn, P., Alias, Y., & Manan, N. S. (2015). One-step hydrothermal green synthesis of silver nanoparticle-carbon nanotube reduced-graphene oxide composite and its application as hydrogen peroxide sensor. *Sensors and Actuators B: Chemical*, 208, 389-398.
- Lu, X., Zhang, H., Ni, Y., Zhang, Q., & Chen, J. (2008). Porous nanosheet-based ZnO microspheres for the construction of direct electrochemical biosensors. *Biosensors and Bioelectronics*, 24(1), 93-98.

- Luo, X., Killard, A. J., Morrin, A., & Smyth, M. R. (2006). Enhancement of a conducting polymer-based biosensor using carbon nanotube-doped polyaniline. *Analytica chimica acta*, 575(1), 39-44.
- Luo, Y.-C., & Do, J.-S. (2004). Urea biosensor based on PANi (urease)-Nafion®/Au composite electrode. *Biosensors and Bioelectronics*, 20(1), 15-23.
- Ma, H., Xue, N., Li, Z., Xing, K., & Miao, X. (2018). Ultrasensitive detection of miRNA-155 using multi-walled carbon nanotube-gold nanocomposites as a novel fluorescence quenching platform. *Sensors and Actuators B: Chemical*.
- Magar, H. S., Ghica, M. E., Abbas, M. N., & Brett, C. M. (2017). A novel sensitive amperometric choline biosensor based on multiwalled carbon nanotubes and gold nanoparticles. *Talanta*, 167, 462-469.
- Mohanty, S. P., & Kougianos, E. (2006). Biosensors: a tutorial review. *Ieee Potentials*, 25(2), 35-40.
- Morrin, A., Guzman, A., Killard, A. J., Pingarron, J. M., & Smyth, M. R. (2003). Characterisation of horseradish peroxidase immobilisation on an electrochemical biosensor by colorimetric and amperometric techniques. *Biosensors and Bioelectronics*, 18(5-6), 715-720.
- Moyo, M., Okonkwo, J. O., & Agyei, N. M. (2014). An amperometric biosensor based on horseradish peroxidase immobilized onto maize tassel-multi-walled carbon nanotubes modified glassy carbon electrode for determination of heavy metal ions in aqueous solution. *Enzyme and Microbial Technology*, 56, 28-34.
- Naderi Asrami, P., Mozaffari, S. A., Saber Tehrani, M., & Aberoomand Azar, P. (2018). A novel impedimetric glucose biosensor based on immobilized glucose oxidase on a CuO-Chitosan nanobiocomposite modified FTO electrode. *International Journal of Biological Macromolecules*, 118, 649-660.
- Narwal, V., Yadav, N., Thakur, M., & Pundir, C. S. (2017). An amperometric H₂O₂ biosensor based on hemoglobin nanoparticles immobilized on to a gold electrode. *Bioscience Reports*, 37(4), BSR20170194.
- Osuntokun, J., Onwudiwe, D. C., & Ebenso, E. E. (2017). Biosynthesis and Photocatalytic Properties of SnO₂ Nanoparticles Prepared Using Aqueous Extract of Cauliflower. *Journal of Cluster Science*, 28(4), 1883-1896.
- Palanisamy, S., Karuppiah, C., & Chen, S.-M. (2014). Direct electrochemistry and electrocatalysis of glucose oxidase immobilized on reduced graphene oxide and silver nanoparticles nanocomposite modified electrode. *Colloids and Surfaces B: Biointerfaces*, 114, 164-169.

- Pop, E., Mann, D., Wang, Q., Goodson, K., & Dai, H. (2006). Thermal conductance of an individual single-wall carbon nanotube above room temperature. *Nano letters*, 6(1), 96-100.
- Popov, V. N. (2004). Carbon nanotubes: properties and application. *Materials Science and Engineering: R: Reports*, 43(3), 61-102.
- Ren, Q.-Q., Wu, J., Zhang, W.-C., Wang, C., Qin, X., Liu, G.-C., Li, Z.-X., & Yu, Y. (2017). Real-time in vitro detection of cellular H₂O₂ under camptothecin stress using horseradish peroxidase, ionic liquid, and carbon nanotube-modified carbon fiber ultramicroelectrode. *Sensors and Actuators B: Chemical*, 245(Supplement C), 615-621.
- Ren, X., Meng, X., Chen, D., Tang, F., & Jiao, J. (2005). Using silver nanoparticle to enhance current response of biosensor. *Biosensors and Bioelectronics*, 21(3), 433-437.
- Rivero, P. J., Ibañez, E., Goicoechea, J., Urrutia, A., Matias, I. R., & Arregui, F. J. (2017). A self-referenced optical colorimetric sensor based on silver and gold nanoparticles for quantitative determination of hydrogen peroxide. *Sensors and Actuators B: Chemical*, 251, 624-631.
- Santos, A. S., Pereira, A. C., Sotomayor, M. D., Tarley, C. R., Durán, N., & Kubota, L. T. (2007). Determination of Phenolic Compounds Based on Co-Immobilization of Methylene Blue and HRP on Multi-Wall Carbon Nanotubes. *Electroanalysis*, 19(5), 549-554.
- Shahrokhian, S., Salimian, R., & Kalhor, H. R. (2016). A simple label-free electrochemical DNA biosensor based on carbon nanotube–DNA interaction. *RSC Advances*, 6(19), 15592-15598.
- Sheng, Q.-L., Zheng, J.-B., Shang-Guan, X.-D., Lin, W.-H., Li, Y.-Y., & Liu, R.-X. (2010). Direct electrochemistry and electrocatalysis of heme-proteins immobilized in porous carbon nanofiber/room-temperature ionic liquid composite film. *Electrochimica Acta*, 55(9), 3185-3191.
- Sheng, Q., Tang, H., Wang, Y., & Zheng, J. (2016). Direct Electrochemistry of Hemoglobin Based on Silver Sulfide Nanospheres Anchored Multiwalled Carbon Nanotubes. *Journal of The Electrochemical Society*, 163(2), H128-H132.
- Su, Y., Zhou, X., Long, Y., & Li, W. (2018). Immobilization of horseradish peroxidase on amino-functionalized carbon dots for the sensitive detection of hydrogen peroxide. *Microchimica acta*, 185(2), 114.
- Sun, D., Li, H., Li, M., Li, C., Dai, H., Sun, D., & Yang, B. (2018). Electrodeposition synthesis of a NiO/CNT/PEDOT composite for simultaneous detection of

- dopamine, serotonin, and tryptophan. *Sensors and Actuators B: Chemical*, 259, 433-442.
- Sun, Y., He, K., Zhang, Z., Zhou, A., & Duan, H. (2015). Real-time electrochemical detection of hydrogen peroxide secretion in live cells by Pt nanoparticles decorated graphene-carbon nanotube hybrid paper electrode. *Biosensors and Bioelectronics*, 68, 358-364.
- Tao, H., Wang, J., Ou, Y., Zhu, W., Ling, H., Fang, W., & Tu, D. (2014). Construction and Direct Electrochemistry of Hemoglobin-Intercalated Titanate Nanosheets. *Nanoscience and Nanotechnology Letters*, 6(2), 99-105.
- Terse-Thakoor, T., Komori, K., Ramnani, P., Lee, I., & Mulchandani, A. (2015). Electrochemically Functionalized Seamless Three-Dimensional Graphene-Carbon Nanotube Hybrid for Direct Electron Transfer of Glucose Oxidase and Bioelectrocatalysis. *Langmuir*, 31(47), 13054-13061.
- Thandavan, K., Gandhi, S., Nesakumar, N., Sethuraman, S., Rayappan, J. B. B., & Krishnan, U. M. (2015). Hydrogen peroxide biosensor utilizing a hybrid nano-interface of iron oxide nanoparticles and carbon nanotubes to assess the quality of milk. *Sensors and Actuators B: Chemical*, 215, 166-173.
- Thenmozhi, K., & Narayanan, S. S. (2017). Horseradish peroxidase and toluidine blue covalently immobilized leak-free sol-gel composite biosensor for hydrogen peroxide. *Materials Science and Engineering: C*, 70, 223-230.
- Thévenot, D. R., Toth, K., Durst, R. A., & Wilson, G. S. (2001). Electrochemical biosensors: recommended definitions and classification. International Union of Pure and Applied Chemistry: Physical Chemistry Division, Commission I.7 (Biophysical Chemistry); Analytical Chemistry Division, Commission V.5 (Electroanalytical Chemistry).1. *Biosensors and Bioelectronics*, 16(1), 121-131.
- Valcárcel, M., Cárdenas, S., & Simonet, B. (2007). Role of carbon nanotubes in analytical science. *Analytical chemistry*, 79(13), 4788-4797.
- Veitch, N. C. (2004). Horseradish peroxidase: a modern view of a classic enzyme. *Phytochemistry*, 65(3), 249-259.
- Vilian, A. E., Chen, S.-M., Kwak, C. H., Hwang, S.-K., Huh, Y. S., & Han, Y.-K. (2016). Immobilization of hemoglobin on functionalized multi-walled carbon nanotubes-poly-l-histidine-zinc oxide nanocomposites toward the detection of bromate and H₂O₂. *Sensors and Actuators B: Chemical*, 224, 607-617.
- Wali, Q., Fakharuddin, A., Ahmed, I., Ab Rahim, M. H., Ismail, J., & Jose, R. (2014a). Multiporous nanofibers of SnO₂ by electrospinning for high efficiency dye-sensitized solar cells. *Journal of Materials Chemistry A*, 2(41), 17427-17434.

- Wali, Q., Fakharuddin, A., Ahmed, I., Ab Rahim, M. H., Ismail, J., & Jose, R. (2014b). Multiporous nanofibers of SnO₂ by electrospinning for high efficiency dye-sensitized solar cells. *Journal of Materials Chemistry A*, 2(41), 17427-17434.
- Wali, Q., Fakharuddin, A., & Jose, R. (2015). Tin oxide as a photoanode for dye-sensitized solar cells: Current progress and future challenges. *Journal of Power Sources*, 293, 1039-1052.
- Wang, F., Yang, C., Duan, M., Tang, Y., & Zhu, J. (2015). TiO₂ nanoparticle modified organ-like Ti₃C₂ MXene nanocomposite encapsulating hemoglobin for a mediator-free biosensor with excellent performances. *Biosensors and Bioelectronics*, 74, 1022-1028.
- Wang, J. (2006). *Analytical electrochemistry*: John Wiley & Sons.
- Wang, M.-Q., Zhang, Y., Bao, S.-J., Yu, Y.-N., & Ye, C. (2016). Ni (II)-based metal-organic framework anchored on carbon nanotubes for highly sensitive non-enzymatic hydrogen peroxide sensing. *Electrochimica Acta*, 190, 365-370.
- Wang, Y.-H., Zhang, F., Miao, P., Zhao, J.-L., Yu, C.-M., Gu, H.-Y., & Tu, Y.-F. (2017). Highly sensitive amperometric biosensor based on AP@ Hb for the detection of 1-pyrene butyric acid. *Sensors and Actuators B: Chemical*, 250, 139-146.
- Wang, Y., Chen, X., & Zhu, J.-J. (2009). Fabrication of a novel hydrogen peroxide biosensor based on the AuNPs-C@SiO₂ composite. *Electrochemistry communications*, 11(2), 323-326.
- Wasik, D., Mulchandani, A., & Yates, M. V. (2017). A heparin-functionalized carbon nanotube-based affinity biosensor for dengue virus. *Biosensors and Bioelectronics*, 91, 811-816.
- Wei, C., Wang, S., Li, J., Liao, C., Chen, B., & Zhou, Q. (2016). *Sensing properties of NiO@ SnO₂ based sensor to hydrogen extracted from transformer oil*. Paper presented at the High Voltage Engineering and Application (ICHVE), 2016 IEEE International Conference on.
- Wen, Y., Wen, W., Zhang, X., & Wang, S. (2016). Highly sensitive amperometric biosensor based on electrochemically-reduced graphene oxide-chitosan/hemoglobin nanocomposite for nitromethane determination. *Biosensors and Bioelectronics*, 79, 894-900.
- Wijeratne, K., Akilavasan, J., Thelakkat, M., & Bandara, J. (2012). Enhancing the solar cell efficiency through pristine 1-dimentional SnO₂ nanostructures: Comparison of charge transport and carrier lifetime of SnO₂ particles vs. nanorods. *Electrochimica Acta*, 72, 192-198.

- Willner, I., Katz, E., & Willner, B. (1997). Electrical contact of redox enzyme layers associated with electrodes: routes to amperometric biosensors. *Electroanalysis*, 9(13), 965-977.
- Wu, C., Liu, Z., Sun, H., Wang, X., & Xu, P. (2016). Selective determination of phenols and aromatic amines based on horseradish peroxidase-nanoporous gold co-catalytic strategy. *Biosensors and Bioelectronics*, 79, 843-849.
- Xie, L., Xu, Y., & Cao, X. (2013). Hydrogen peroxide biosensor based on hemoglobin immobilized at graphene, flower-like zinc oxide, and gold nanoparticles nanocomposite modified glassy carbon electrode. *Colloids and Surfaces B: Biointerfaces*, 107, 245-250.
- Xu, Q., Gu, S.-X., Jin, L., Zhou, Y.-e., Yang, Z., Wang, W., & Hu, X. (2014). Graphene/polyaniline/gold nanoparticles nanocomposite for the direct electron transfer of glucose oxidase and glucose biosensing. *Sensors and Actuators B: Chemical*, 190, 562-569.
- Xu, Q., Mao, C., Liu, N.-N., Zhu, J.-J., & Sheng, J. (2006). Direct electrochemistry of horseradish peroxidase based on biocompatible carboxymethyl chitosan-gold nanoparticle nanocomposite. *Biosensors and Bioelectronics*, 22(5), 768-773.
- Xu, S.-X., Li, J.-L., Zhou, Z.-L., & Zhang, C.-X. (2014). A third-generation hydrogen peroxide biosensor based on horseradish peroxidase immobilized by sol-gel thin film on a multi-wall carbon nanotube modified electrode. *Analytical Methods*, 6(16), 6310-6315.
- Xu, S., Qin, X., Zhang, X., & Zhang, C. (2015a). A third-generation biosensor for hydrogen peroxide based on the immobilization of horseradish peroxidase on a disposable carbon nanotubes modified screen-printed electrode. *Microchimica acta*, 182(7-8), 1241-1246.
- Xu, S., Qin, X., Zhang, X., & Zhang, C. (2015b). A third-generation biosensor for hydrogen peroxide based on the immobilization of horseradish peroxidase on a disposable carbon nanotubes modified screen-printed electrode. *Microchimica acta*, 182(7), 1241-1246.
- Yang, N., Chen, X., Ren, T., Zhang, P., & Yang, D. (2015). Carbon nanotube based biosensors. *Sensors and Actuators B: Chemical*, 207, 690-715.
- Yang, Y., Asiri, A. M., Du, D., & Lin, Y. (2014). Acetylcholinesterase biosensor based on a gold nanoparticle-polypyrrole-reduced graphene oxide nanocomposite modified electrode for the amperometric detection of organophosphorus pesticides. *Analyst*, 139(12), 3055-3060.

- Yi, X., Huang-Xian, J., & Hong-Yuan, C. (2000). Direct Electrochemistry of Horseradish Peroxidase Immobilized on a Colloid/Cysteamine-Modified Gold Electrode. *Analytical biochemistry*, 278(1), 22-28.
- Yu, Y., Chen, Z., He, S., Zhang, B., Li, X., & Yao, M. (2014). Direct electron transfer of glucose oxidase and biosensing for glucose based on PDDA-capped gold nanoparticle modified graphene/multi-walled carbon nanotubes electrode. *Biosensors and Bioelectronics*, 52, 147-152.
- Zhang, B., Zhou, J., Li, S., Zhang, X., Huang, D., He, Y., Wang, M., Yang, G., & Shen, Y. (2015). Hydrogen peroxide biosensor based on microperoxidase-11 immobilized on flexible MWCNTs-BC nanocomposite film. *Talanta*, 131, 243-248.
- Zhang, L., Han, G., Liu, Y., Tang, J., & Tang, W. (2014). Immobilizing haemoglobin on gold/graphene–chitosan nanocomposite as efficient hydrogen peroxide biosensor. *Sensors and Actuators B: Chemical*, 197, 164-171.
- Zhang, M.-R., Chen, X.-Q., & Pan, G.-B. (2017). Electrosynthesis of gold nanoparticles/porous GaN electrode for non-enzymatic hydrogen peroxide detection. *Sensors and Actuators B: Chemical*, 240, 142-147.
- Zhao, Y.-D., Zhang, W.-D., Chen, H., Luo, Q.-M., & Li, S. F. Y. (2002). Direct electrochemistry of horseradish peroxidase at carbon nanotube powder microelectrode. *Sensors and Actuators B: Chemical*, 87(1), 168-172.
- Zheng, X., Zhu, Q., Song, H., Zhao, X., Yi, T., Chen, H., & Chen, X. (2015). In Situ Synthesis of Self-Assembled Three-Dimensional Graphene–Magnetic Palladium Nanohybrids with Dual-Enzyme Activity through One-Pot Strategy and Its Application in Glucose Probe. *ACS applied materials & interfaces*, 7(6), 3480-3491.
- Zhu, H., Xu, C., Wu, D., Wei, B., Vajtai, R., & Ajayan, P. (2002). Direct synthesis of long single-walled carbon nanotube strands. *Science*, 296(5569), 884-886.
- Zhu, J., Liu, X., Wang, X., Huo, X., & Yan, R. (2015). Preparation of polyaniline–TiO₂ nanotube composite for the development of electrochemical biosensors. *Sensors and Actuators B: Chemical*, 221, 450-457.
- Zhu, L., Yang, R., Zhai, J., & Tian, C. (2007). Bionzymatic glucose biosensor based on co-immobilization of peroxidase and glucose oxidase on a carbon nanotubes electrode. *Biosensors and Bioelectronics*, 23(4), 528-535.
- Zhu, Z., Qu, L., Niu, Q., Zeng, Y., Sun, W., & Huang, X. (2011). Urchinlike MnO₂ nanoparticles for the direct electrochemistry of hemoglobin with carbon ionic liquid electrode. *Biosensors and Bioelectronics*, 26(5), 2119-2124.